

Deactivation of Promoted Co Alumina Catalysts for Fischer Tropsch Synthesis

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Beamline: X18B

Introduction: Decreasing the deactivation rates of Fischer Tropsch synthesis (FTS) catalysts has been one of the important challenges facing the development of these catalysts for the conversion of coal and natural gas to liquid fuels as alternative resources to crude oil. One important option being considered includes the combination of a highly active and stable Co-alumina catalyst and a slurry phase or slurry bubble column reactor. Alumina is an appropriate choice due to its attrition resistance. However, one fundamental problem facing the development of Co-alumina catalysts is the strong interaction between the support and cobalt oxide species, which impede their reduction during activation. Therefore, small quantities of promoter metals such as Pt, Ru, or Re are added to improve their reducibility [1]. We have tested 15% loaded Co catalysts with each promoter and found that while the catalyst exhibits improved initial activity, due to the accessing of additional active sites, the catalysts deactivate more rapidly than their unpromoted counterparts [2].

Methods and Materials: We developed a technique where we can remove directly from the continuously stirred tank reactor (CSTR) samples of catalyst within the solid wax product for XAFS analysis. This allows us to examine samples as a function of reactor time onstream. Samples were pressed in the wax and scanned in a XAFS cell cooled to liquid nitrogen temperature under helium flow.

Results: Results from a study of a 0.2%Re promoted 15%Co alumina catalyst indicated that the deactivation of the catalyst likely involves two processes. Temperature programmed reduction (TPR) indicated that the promoter catalyzed the reduction of Co species interacting with the alumina support, as shown in Figure 1. Results of hydrogen chemisorption/pulse reoxidation indicated that the small cobalt metal clusters accessed by the noble metal promoter caused a decrease in the average Co cluster size in comparison with the unpromoted catalyst from 5.9 nm to 5.1 nm. As shown in Figure 2, the catalyst

undergoes significant initial deactivation. The arrows indicate points where catalyst was removed from the CSTR for XAFS analysis. EXAFS of the samples removed from the reactor with time onstream indicated that these small Co metal clusters underwent a gradual sintering process, as observed in an augmentation of the Chi function and a gradual increase in the FT magnitude of the Co-Co shells with reactor time onstream, demonstrated in Figure 3. Atoms [3], FEFF [4], and FEFFIT [4] were used to fit the first shell of the Co-Co contribution, as displayed in Figure 3. Earlier studies by others [5] indicated that these very small clusters may deviate from bulklike behavior and undergo reoxidation under FTS as the main cause of deactivation. Thermodynamically, the reoxidation of Co metal is not allowed under the partial pressures of water experienced during normal FTS conditions. Interestingly, examination of our XANES spectra in Figure 4 for the most deactivated catalysts did show a small contribution from an oxidized state of Co. A linear combination fit of reference compounds indicated that the contribution may be a cobalt aluminate phase.

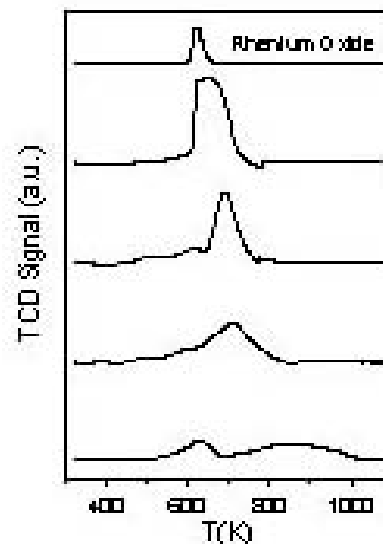


Figure 1: Comparative TPR spectra of unpromoted (bottom) 15%Co/Al₂O₃ catalyst with those promoted with (moving up) 0.2%, 0.5%, and 1.0% Re. Top spectra is the reduction of Re₂O₇ precursor (unsupported).

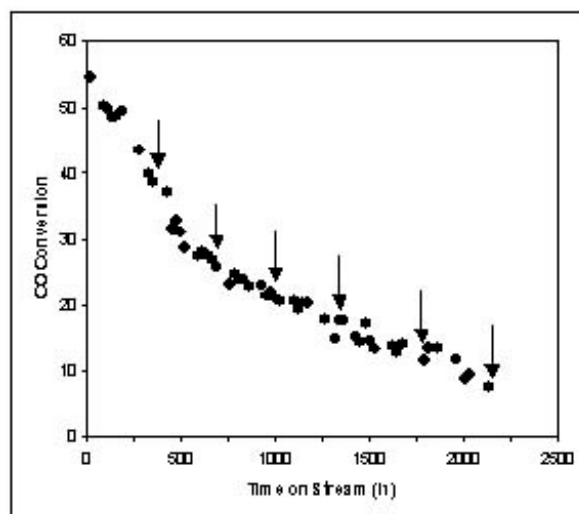


Figure 2: Deactivation of a 0.2%Re promoted 15%Co alumina FTS catalyst. Arrows indicate points where catalyst was removed for XAFS analysis.

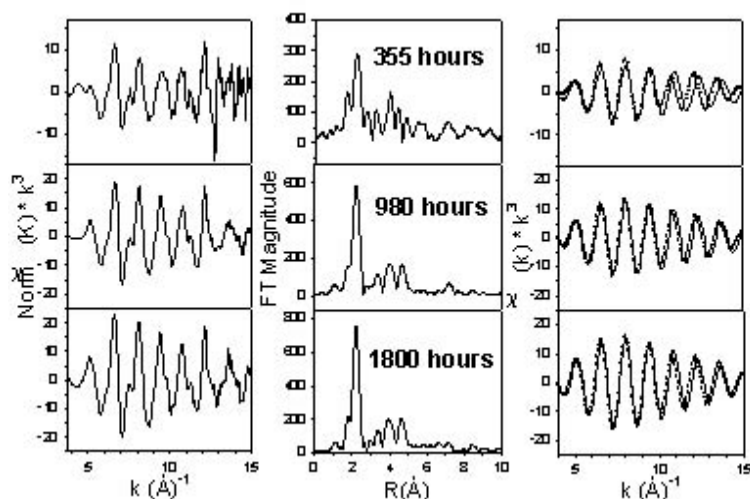


Figure 3: EXAFS results $c(k)k^3$ vs k , the Fourier transform magnitude, and first shell inverse transforms for used 0.2%Re-15%Co/ γ - Al_2O_3 sampled during deactivation at 355, 980, and 1800 hours onstream, respectively. The solid lines represent the inverse transform, while the plotted points indicate the fit by FEFFIT. Below shows a table of the fitting parameters determined by FEFFIT.

Sample	N_1	ΔN_1	E_0	ΔE_0	σ^2	$\Delta \sigma^2$	ΔE_{Feff}	$\Delta \Delta E_{\text{Feff}}$	χ -factor
355 hours	2.48	0.43	2.54	1.94	0.00339	0.00133	-0.0258	0.0120	0.115
445 hours	3.47	0.37	3.10	1.27	0.00422	0.00093	-0.0214	0.00808	0.045
980 hours	5.41	0.28	5.49	0.59	0.00389	0.00043	-0.0144	0.00373	0.018
1340 hours	6.50	0.32	7.21	0.57	0.00399	0.00043	-0.00473	0.00348	0.017
1800 hours	7.54	0.27	7.74	0.41	0.00455	0.00032	-0.00407	0.00248	0.0088
2135 hours	7.45	0.34	7.70	0.50	0.00500	0.00041	-0.00303	0.00339	0.013

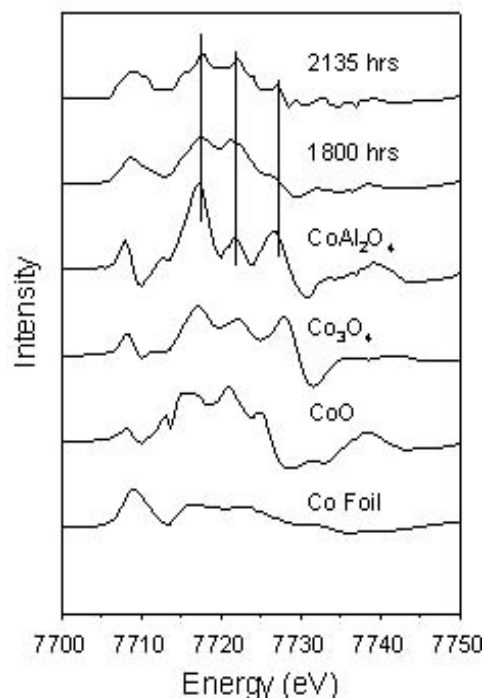


Figure 4: XANES derivative spectra (right) of the used catalyst after deactivation time of 1800 hours and 2135 hours in the Fischer-Tropsch Synthesis CSTR reactor versus those of comparative standards, including Co metal foil, Co_3O_4 , CoO , and CoAl_2O_4 .

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